

Response to “Comment on ‘Residual multiparticle entropy does not generally change sign near freezing’ ”

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The residual multiparticle entropy (RMPE) changes sign under conditions very close to the freezing transition for several three-dimensional models of simple fluids (see, e.g., Refs. 1 and 2), an observation that forms the basis of the zero-RMPE freezing criterion. The fact that a single structural property of one phase seems to empirically “predict” a nearby equilibrium between two coexisting phases in these systems is surprising and deserves more careful scrutiny. Does the apparent coincidence of the zero-RMPE point and the freezing line imply that there is a fundamental connection between the structural changes that the RMPE measures and the emergence of the phase transition? Will the zero-RMPE criterion generally serve as good empirical rule for forecasting the location of the freezing transition of other systems? In Ref. 3, we took what we felt was an obvious step toward addressing those questions by investigating the behavior of a class of basic model systems: Equilibrium hard spheres in spatial dimension d . We used exact results to study the $d=1$ case, computer simulations for $d=2-5$, and approximate theoretical predictions for $d \rightarrow \infty$. The behaviors of these systems demonstrate that, as perhaps should be expected, a change in sign of the RMPE of the fluid is not always a reliable locator of the freezing transition.

Specifically, the equilibrium hard-sphere fluid exhibits a zero-RMPE point in $d=1$ even though that system does not exhibit a freezing transition (i.e., if strictly interpreted as a freezing rule, the criterion produces a “false positive”).³ The zero-RMPE point occurs below the freezing density in $d=2$, while it nearly coincides with the freezing density in $d=3$. Only lower bounds to the zero-RMPE point could be obtained by simulations in $d=4$ and $d=5$,³ but even these bounds occur at densities that are significantly above computer simulation estimates^{4,5} for the freezing densities. The “overpredictions” of the freezing density for $d > 3$ suggest the possibility that high-dimensional hard-sphere fluids may even encounter the glass transition upon densification before reaching the zero-RMPE point. As we discussed in Ref. 3, that scenario, while currently impossible to rigorously verify, is at least consistent with recent theoretical predictions⁶⁻⁸ for the behavior of the hard-sphere fluid as $d \rightarrow \infty$.

In his Comment,⁹ Giaquinta correctly noted that our analysis for $d=4$ and $d=5$ hinges on knowledge of the approximate location of the freezing transitions for these systems. Moreover, as he pointed out, the most recent computer simulation estimates for the freezing transition in $d=4$ and $d=5$ referred to in our work were not based on the rigorous thermodynamic requirement of equality of chemical potential and pressure of two phases at the same temperature.^{4,5} Rather, as discussed in Ref. 4, the freezing density was assumed to coincide with the low-density limit of mechanical stability of the “undercompressed” crystal—a computationally convenient heuristic based on the known freezing behavior of fluids in lower spatial dimensions.⁵ The crux of Giaquinta’s argument is that, since the estimates of the freezing density were not obtained from rigorous methods, there still exists the possibility that the actual freezing densities in $d=4$ and $d=5$ will be considerably higher than the estimates we used in Ref. 3 and thus even perhaps consistent with the predictions of the zero-RMPE freezing criterion.

We now know, however, that this hypothetical scenario does not occur in $d=4$. Since the publication of our manuscript, a careful simulation study has been performed in which the appropriate thermodynamic criterion was used to accurately determine the freezing transition of the $d=4$ hard-sphere fluid.¹⁰ Interestingly, the freezing density obtained by the thermodynamic method ($\rho_f=0.93$) is *lower* than the earlier heuristic estimate^{4,5} we reported in our paper ($\rho_f=1.04$). In other words, the failure of the zero-RMPE criterion in $d=4$ fluid is actually *more pronounced* than what we originally reported. It overpredicts the freezing density by more than 30% in $d=4$, as opposed to the milder 18% overprediction we reported in Ref. 3. Aside from the significant quantitative failure of the zero-RMPE “prediction” of the freezing density in this case, we find it difficult to believe that any structural change that happens at a density 30% larger than the freezing density is intimately connected to freezing.

Unfortunately, the freezing density of the $d=5$ system is not yet known with certainty. Clearly, if the heuristic system used in Refs. 4 and 5 for the $d=4$ system similarly overestimates the freezing density in $d=5$, then the failure of the zero-RMPE

criterion in that case will also be worse than what we reported in Ref. 3. We look forward to a rigorous thermodynamic analysis of the $d=5$ hard-sphere freezing transition to determine if that is indeed the case.

As far as the $d=1$ fluid is concerned, Giaquinta claimed that the change in sign of the RMPE, while not strictly signaling a freezing transition, still has physical relevance. Specifically, he argued that the fluid forms a “pseudocrystalline state consisting of a quasi regularly spaced sequence of particles” by a process which “builds up gradually with increasing densities and, according to different concurrent indications, culminates with the formation of a solidlike arrangement in the close neighborhood of...” the zero-RMPE point. We remain unconvinced that it is meaningful to describe the aforementioned gradual changes in the equilibrium fluid as the onset of “solidlike” structure, but we encourage readers to examine Giaquinta’s recent paper about this system¹¹ in order to form their own judgment about the merits of that view.

We conclude by noting that it was the coincidence in $d=3$ (and the near coincidence in $d=2$) of the zero-RMPE point and the freezing density which originally suggested that the change in sign of the RMPE had important implications for the behaviors of these systems. However, the data in Ref. 3, supplemented by the discussion above, show that this coincidence is not general, which calls into question whether there is any fundamental relationship between the structural order measured by the RMPE and the freezing transition. In

the absence of a connection to freezing, we fail to appreciate the “special physical significance” of the zero-RMPE point for the hard-sphere fluid.

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¹P. V. Giaquinta and G. Giunta, *Physica A* **187**, 145 (1992).

²P. V. Giaquinta, G. Giunta, and S. Prestipino Giarratta, *Phys. Rev. A* **45**, R6966 (1992).

³W. P. Krekelberg, V. K. Shen, J. R. Errington, and T. M. Truskett, *J. Chem. Phys.* **128**, 161101 (2008).

⁴M. Skoge, A. Donev, F. H. Stillinger, and S. Torquato, *Phys. Rev. E* **74**, 041127 (2006).

⁵J. P. J. Michels and N. J. Trappeniers, *Phys. Lett. A* **104**, 425 (1984).

⁶G. Parisi and F. Slanina, *Phys. Rev. E* **62**, 6554 (2000).

⁷G. Parisi and F. Zamponi, *J. Stat. Mech.: Theory Exp.*, P03017 (2006).

⁸F. Zamponi, *Philos. Mag.* **87**, 485 (2007).

⁹P. V. Giaquinta, *J. Chem. Phys.* **130**, 037101 (2009).

¹⁰J. van Meel, D. Frenkel, and P. Charbonneau, e-print arXiv:0809.1775v1 (2008).

¹¹P. V. Giaquinta, *Entropy* **10**, 248 (2008).